


# Revealing the Mysteries of Water

*Armed with Livermore's  
supercomputing capability  
and new algorithms,  
researchers are unveiling  
properties of this common  
but complex substance.*





**W**ATER would seem to be relatively easy for scientists to understand. It is the only natural substance on Earth that is found as a gas, liquid, and solid. It covers 70 percent of Earth's surface, makes up 60 percent of the human body, and constitutes 90 percent of a person's blood.

However, the water molecule is far from simple. Given its low molecular weight, water at ambient conditions should be a gas instead of a liquid. Its boiling point is nearly 200°C higher than expected compared with similar-size molecules. And, unlike most substances, when ice melts, the water molecules pack more closely together than they do when frozen, which is why ice cubes float. In addition to its familiar liquid phase, water has at least 3 other liquidlike phases and up to 14 solid phases.

Water's unusual properties have unexpected effects on the thermodynamic behavior of its phases. For example,

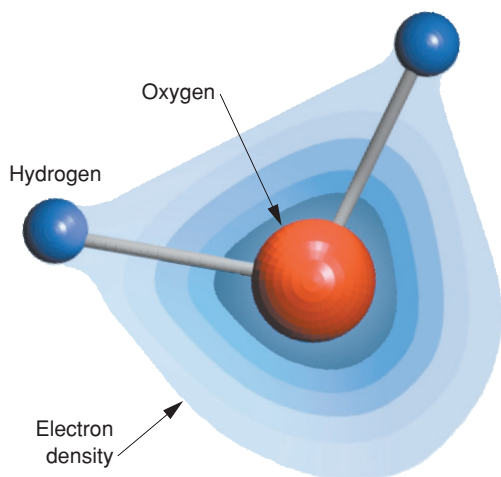
temperature and pressure affect the molecules differently when water approaches its boiling point than when it is close to freezing. Heating already hot water increases its isothermal compressibility and heat capacity and reduces its density, but heating cold water has the opposite effect. Also, applying pressure reduces the mobility of the molecules in hot water but increases their mobility in cold water. Ice melts when slight pressure is applied, but under high pressure, liquid freezes.

Understanding water is important to a range of research areas from geosciences to biological systems to astrophysics. But explaining the anomalous properties of this mysterious molecule has challenged both theorists and experimentalists. Scientists began to simulate liquid water almost 40 years ago. Yet, they continue to pursue more accurate models so they can better analyze this surprisingly complex molecule.

The revolution in supercomputing has been a boon to such research. To simulate even a few hundred atoms requires supercomputing capabilities, such as those available with Livermore's unclassified supercomputer, Thunder. Funded by the Laboratory's Multiprogrammatic and Institutional Computing Initiative, Thunder can process 23 trillion operations per second. In June 2005, it ranked seventh on the Top500 List, the leading industry authority for high-performance computing.

By designing algorithms to exploit Thunder's capabilities, a team of Livermore researchers, led by chemist Christopher Mundy, has made important contributions to the study of water and its properties. With funding from the Laboratory Directed Research and Development Program, Mundy's team examined the behavior of water at the molecular level under changing conditions. The team's models reproduced





The average electron density around the oxygen atom in a water molecule is about 10 times that around the hydrogen atoms. This nonuniform distribution of positive and negative charges leads to the substance's unusual behavior.

the bulk properties of liquid water. With this improved capability, researchers can better understand the many phases of water and predict the behavior of more complex molecular fluids.

### A First-Principles Approach to Water

The basis of water's unexpected properties is the electronic structure of the oxygen atom and the two hydrogen atoms that make up the V-shaped molecule. A water molecule's valence electrons (the electrons in the outer shell, which are thus the most reactive) spend more time around the oxygen atom than they do around the hydrogen atoms. Because electrons carry a negative charge, the oxygen end of the molecule develops a partial negative charge, and the hydrogen end of the molecule develops a partial positive charge. This nonuniform distribution of positive and negative charges is called an electric dipole.

The strong dipole present in water leads to its unique behavior. (See the [box](#) below.)

The electrostatic attraction between the hydrogen and oxygen in adjacent molecules creates hydrogen bonding, a weak attractive force. Hydrogen bonds between water molecules are responsible for a tetrahedral structure that gives water many of its unusual properties.

Early simulations used classical molecular dynamics (MD) calculations to examine the liquid phase of water in bulk form. In classical MD, molecules move according to forces that are defined by empirical interaction potentials. These potentials are determined by observing how molecules behave in a given phase at a specific temperature or pressure. By integrating the Newtonian equations of motion, researchers can then compute the trajectory of molecules in small time steps.

A drawback to this method is the narrow range of information it provides because the calculation is specific to a set of parameters. To model the diffusion of a water molecule, researchers must limit the range of temperatures and pressures for the

## A Common Substance with Unusual Properties

Water is indeed strange for a substance at neutral pH, midway between the hazardous acid and alkali extremes. The atoms in a water molecule—two hydrogen and one oxygen—are arranged at the corners of an isosceles triangle. The asymmetrical shape of the molecule occurs because the four electron pairs in the outermost shell of oxygen tend to arrange themselves symmetrically at the vertices of a tetrahedron around the oxygen nucleus. When water molecules are close enough, each oxygen atom attracts the nearby hydrogen atoms of two other water molecules, forming hydrogen bonds. These hydrogen bonds are responsible for many properties of water, some of which are unusual. For example, solids are usually the densest form of a substance, followed by liquids and then gases. As temperature increases, a substance's density generally decreases. But pure water is an exception to this rule—it is the only known substance that has its highest density as a liquid. At low temperatures, water has a higher density than ice, which is why ice floats.

Water has an unusually large heat capacity, requiring a lot of energy to increase its temperature. This characteristic prevents Earth from getting too hot or too cold, and it slows the temperature changes in oceans, biological cells, and tissues, making conditions possible for

life. Water also has a high heat of vaporization, so a lot of energy from the Sun is needed to turn liquid water into vapor. It takes four times as much energy to heat a given mass of water by 1°C as it does to heat the same mass of dry air.

Water's dielectric constant—that is, its tendency to interact with applied electric fields—and its ability to neutralize the attraction between electric charges enables it to buffer or weaken the forces between dissolved ions and molecules. Thus, water is a powerful solvent and a medium for biochemical reactions.

Water is crucial for all life. Liquid water absorbs radiation of all wavelengths, except a narrow window in the visible (photochemical) waveband. This window is critical for photolysis and directly or indirectly influences the development of all life on Earth. Water's high thermal conductivity speeds up heat redistribution in living tissues, which helps protect the body from uneven heating and cooling, whether such changes are caused by metabolic processes or external mechanisms. In biochemical reactions, water plays a passive role as a solvent for minerals, organic solutes, and gases, but it can play an active role in such vital processes as photosynthesis and respiration.

simulation. Water's strong dipole moment and highly directional hydrogen bonds that participate in chemical and physical processes pose a great challenge in defining these parameters for dynamic simulations.

Another drawback is that classical MD does not capture bonds being made and broken. Instead, it approximates the real system by treating the entire molecule as a single unit. These calculations can provide useful information about water at low temperature and pressure, where chemical bonds rarely break. However, to study chemical reactions, especially at extreme temperatures and pressures, researchers need a more fundamental description of water that can only be obtained by a first-principles model.

First-principles MD models do not include assumptions about the characteristics of interatomic and intermolecular interactions. Instead, the models use the laws of quantum mechanics to compute the forces that govern these interactions. These forces can be derived directly from the ground-state electronic structure of the molecules' chemical bonds.

One method used with first-principles models includes quantum mechanics based on density functional theory (DFT). Walter Kohn, a professor at the University of California at Santa Barbara, developed this approach and, in 1998, won a Nobel Prize in Chemistry for his work on DFT. Instead of using the many-body wave function to describe all the electrons in a molecule, DFT defines a molecule's energy and electronic structure in terms of the electron density in the molecule. Electron density is a simpler quantity to handle computationally, especially with a large number of electrons. Once scientists have defined the electronic structure of a material's molecules, they can, in principle, calculate all of the material's chemical and physical properties.

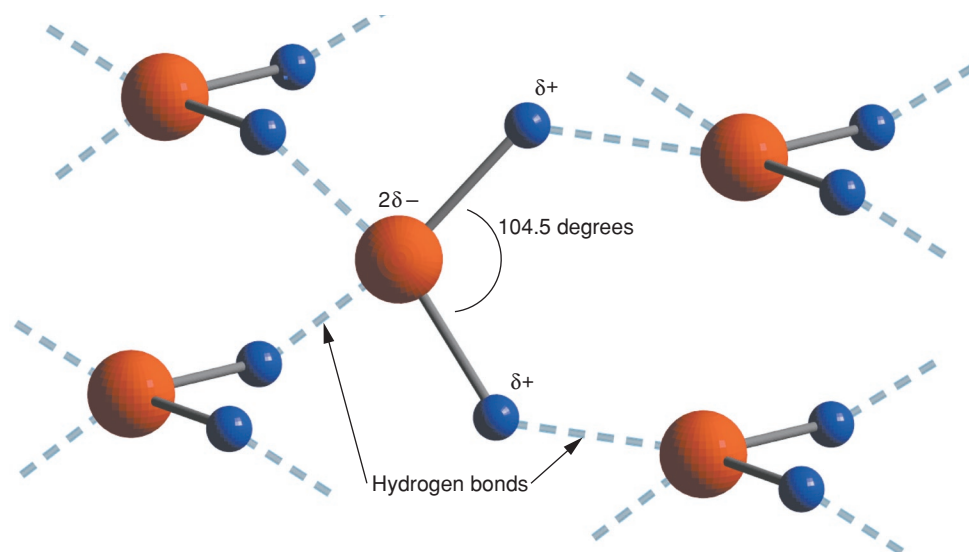
### Finding Stable Phases of Water

To model the trajectories of water molecules, Mundy and his colleagues used a method called Car-Parinello molecular dynamics (CPMD). Developed in 1985 by

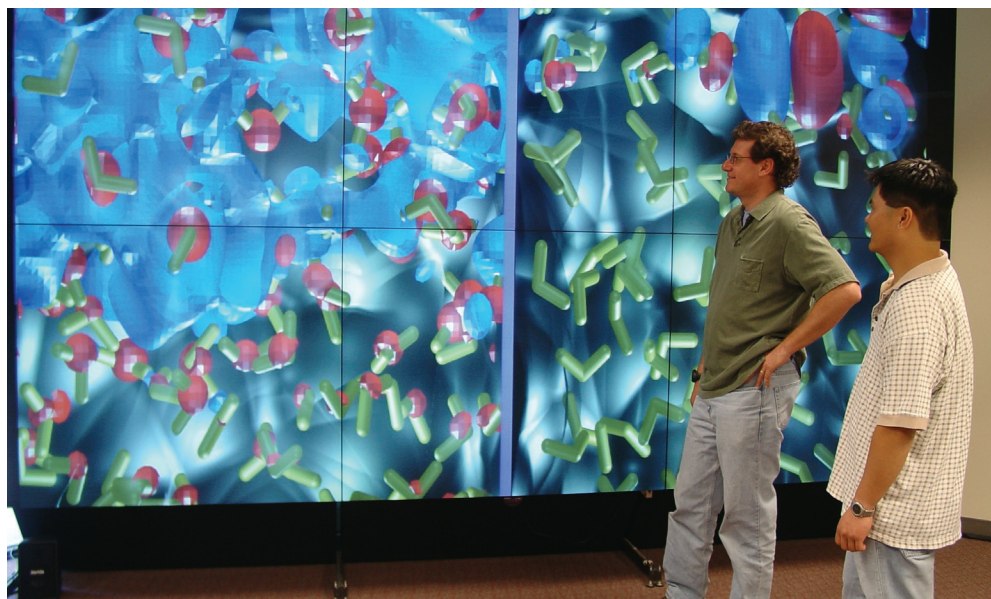
Roberto Car and Michele Parinello, CPMD applies classical Newtonian principles to model nuclei and DFT principles to model electronic structure.

In the early 1990s, when CPMD was first used, computing capability limited the

system being modeled to 32 water molecules and 1 to 2 picoseconds (a picosecond is  $10^{-12}$  seconds). These size and time scales provided insufficient resolution for studying properties that arise from statistically rare interactions. With Thunder's capabilities,



In liquid and solid water, hydrogen (blue) and oxygen (red) molecules form so-called hydrogen bonds between the positive hydrogen atoms ( $\delta+$ ) and negative oxygen atoms ( $\delta-$ ). This bonding results in a relatively strong tetrahedral structure.



Livermore chemists Christopher Mundy (left) and Will Kuo view a simulation of water molecules.



the Livermore team can follow the trajectories of 64 water molecules for more than 10 picoseconds or 216 molecules for about 5 picoseconds.

Mundy's team used CPMD and its successor, CP2K, to model the liquid-vapor coexistence curve in water's phase diagram. A coexistence curve is the boundary that separates two phases in equilibrium, such as the liquid and vapor phases. The model produces a phase diagram—a map showing the regions of pressure, volume, and temperature over which various phases are thermodynamically stable. Until now, no thermodynamic characterization of water could be obtained from first-principles methodologies.

Computing coexistence curves from first principles is important to physical chemistry research. "The phase diagram is central to thermodynamics," says Mundy. "Only by

understanding thermodynamic properties can we properly compare experiments to theory and simulation."

First-principles calculations also provide a means for exploring the properties of water under conditions that are difficult or impossible to attain experimentally. "Having the capability to predict the thermodynamics of water will help us develop more accurate quantum mechanical models," says Mundy. "Once we can demonstrate that our codes accurately model the chemical and physical changes that occur in water, we can use them to fully characterize other complex molecules."

In the water simulations, Mundy's team ran calculations of 64 molecules at 323, 373, 423, 473, and 523 kelvins. Every simulation required 500 cycles. Each of those cycles ran for about 4 hours and

used 192 of Thunder's 4,096 processors. The team then calculated averages from 200 production cycles. The results were in agreement with experiments, yielding two coexisting phases between 323 and 523 kelvins.

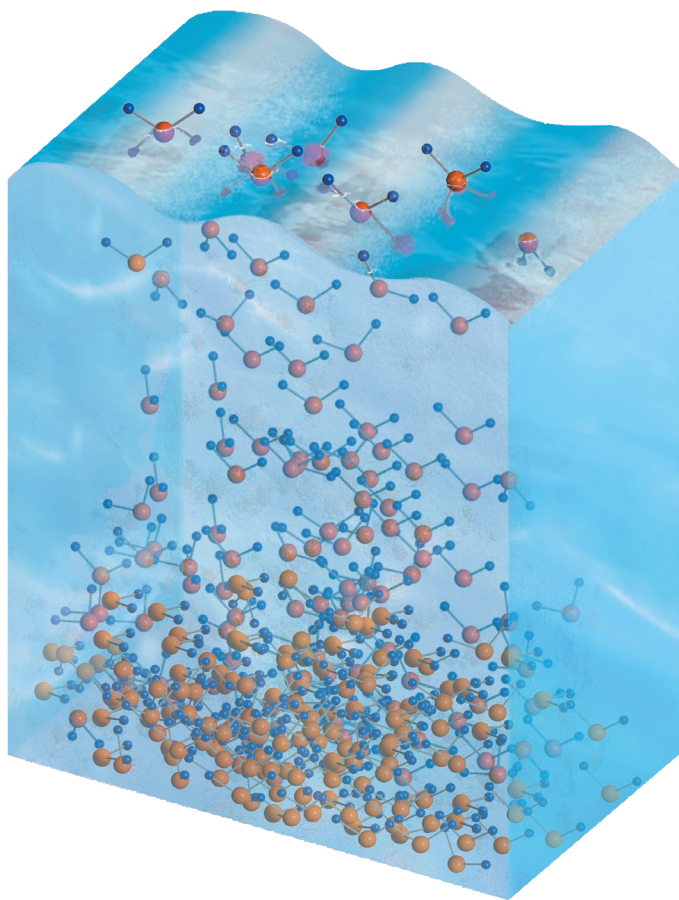
Mundy cautions that, to date, no model of water has been universally accepted. However, he says, "Our code is the first to predict the liquid-vapor coexistence curve using interaction potentials based on density functional theory. That's an important success that supports the Laboratory's national security mission. Many of the chemicals we want to study at Livermore are too hazardous to be tested experimentally. If our codes and models can fully characterize a fluid as complicated as water, we are hopeful that they can be used in Livermore's national security research. We need to better understand the physical and chemical properties of chemical warfare agents that might be used against the U.S. and develop technologies to protect the nation from their use."

### Water's Behavior at the Surface

First-principles simulations also provide a virtual laboratory, allowing researchers to better examine how the structure of water changes at the air-liquid interface. Understanding the thermodynamic properties at the interface of bulk liquid and air is crucial to controlling chemical reactions in various applications, from biology to atmospheric science to homeland security.

For example, scientists have long pondered the orientation of water molecules at the surface of liquid water. They have observed that water's density decreases as it approaches the liquid-vapor interface. The phenomenon, known as surface relaxation, could increase the reactivity of molecules in this interfacial region. Scientists previously believed the interfacial region had an abundance of water molecules whose hydrogen atoms "dangled" or were oriented toward the interface as so-called single donors.

The liquid-air interface of water has an abundance of molecules whose hydrogen atoms are oriented into the air. The phenomenon, known as surface relaxation, may increase the reactivity of molecules in this region of water.



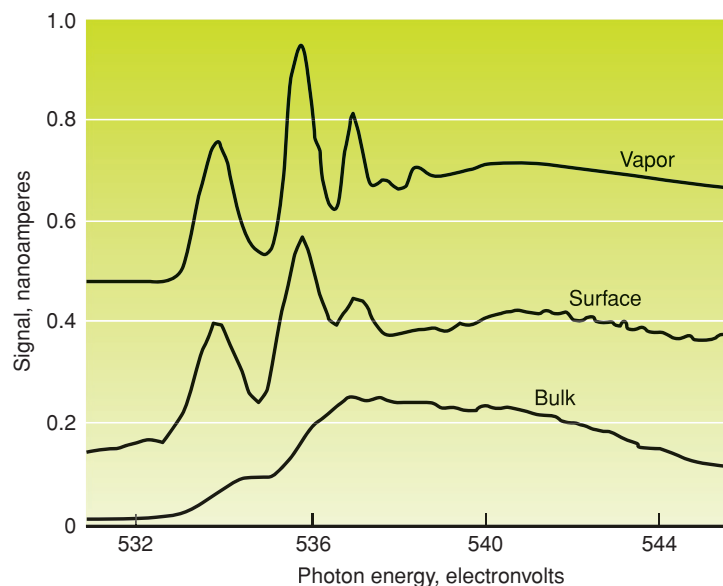


A research collaboration involving Lawrence Livermore and Lawrence Berkeley national laboratories and the University of California at Berkeley provided the first experimental evidence that both hydrogens in a molecule were oriented out of the liquid. (See *S&TR*, November 2001, pp. 20–23.) This team developed a method using extended x-ray absorption fine structure (EXAFS) and near-edge x-ray absorption fine structure (NEXAFS) to probe the water molecule's electronic structure. Previously, x-ray techniques had difficulty characterizing the molecular-scale structure of liquids at interfaces, particularly for liquids containing hydrogen atoms. Another problem was that to perform x-ray spectroscopy, the sample had to be in a vacuum, so the liquid had to be placed behind a barrier. The barrier would interact with the surface of the liquid and absorb most of the x-ray signal.

To overcome these problems, the team replaced the barrier with liquid microjet technology in experiments conducted at Lawrence Berkeley's Advanced Light Source. Using this technology, the team made the first definitive EXAFS measurement on hydrogen and determined that the covalent oxygen–hydrogen bond length in water vapor is  $0.095 \pm 0.003$  nanometer. This research showed that hydrogen bonds could be directly detected in water, paving the way for future studies of intermolecular hydrogen bonds.

In another experiment, NEXAFS spectra obtained for the water surface were intermediate between the spectra for water's bulk and vapor phases. These results indicated that the hydrogen atoms in a large fraction of the water molecules at the interface are not hydrogen-bonded to other molecules. Therefore, they must be oriented outward toward the interface.

Capturing these surface phenomena in theoretical models is more complicated than simulating water in bulk. Livermore chemist Will Kuo explains, "For one thing, we need many more molecules in the system than we do for simulations of bulk water because at



Near-edge x-ray absorption fine structure spectra show the electronic structure of water in vapor form, at the surface of its liquid form, and in its bulk form.

the interface, we are studying particles, such as those released in ocean spray. Therefore, we must account for both interfacial and bulk properties within a single simulation."

To simulate a circular area about 10 nanometers in diameter on the surface of a water droplet, researchers need 216 water molecules—a model size that is three to four times larger than current first-principles MD models of bulk liquid water. Calculations with the CPMD code confirmed that the distance between oxygen molecules increases near the interface, which indicates surface relaxation and an increased potential for chemical reactions relative to bulk water. Kuo says, "The states with the highest energy, which are most likely to be involved in chemical reactions, are clearly located at the surface."

Mundy's team is encouraged by the results, not only for the information they provide about water but also because the methods can be applied to other molecules. "Once we establish the methods to simulate the interface for a system, we can look at any interface to see how the molecules will interact," says Kuo. "The techniques can be used in various applications, from studying environmental toxins to biothreats to biological systems."

## Water in Extreme Conditions

Livermore researchers are also studying the dynamic properties of water under extreme conditions, where water is even more reactive. In one study, Laboratory chemists Larry Fried and Nir Goldman simulated the theoretically predicted superionic phase of water. In this phase, oxygen atoms form a lattice structure, but hydrogen atoms diffuse freely. The predicted superionic phase of water is unusual because it involves elements that form strong covalent bonds under ambient conditions. It is thus a striking example of how extreme pressure can disrupt covalent interactions.

Research indicates that the superionic phase of water could exist in giant planets such as Neptune and Uranus. In fact, scientists speculate that the magnetic field observed emanating from these planets may involve superionic water in the planets' interiors. Water is a highly reactive solid under these conditions. Inside a giant ice planet, superionic water would be hard as steel and would glow yellow at a temperature of more than 2,000 kelvins.

To re-create the extreme conditions inside these planets, Livermore researchers Alex Goncharov, Joe Zaug, and Jonathan Crowhurst compressed samples of ice and

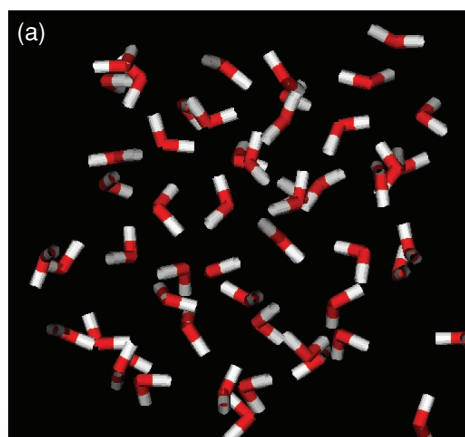


liquid water in a laser-heated diamond anvil cell to pressures between 5 and 56 gigapascals and temperatures between 300 and 1,500 kelvins. Raman spectroscopy indicated a phase transition as temperature and pressure increased.

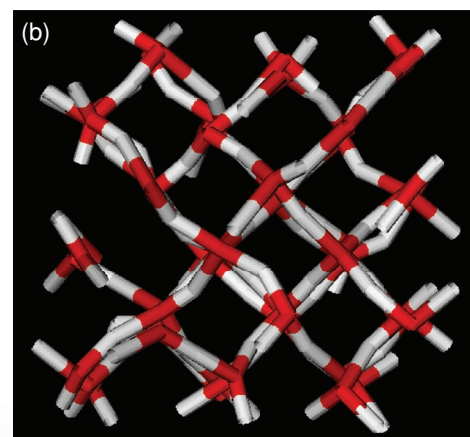
Fried and Goldman then ran the CPMD code on Thunder to simulate the same conditions, modeling a system with 54 water molecules for 5 to 10 picoseconds. In the simulations, they looked at properties such as bond lifetimes, the speed of proton diffusion through the system, and the chemical species present.

Their results explained the phase transition reflected in the Raman spectra. Above 47 gigapascals and 1,000 kelvins, the molecules transition to water's superionic phase. The simulations further showed that from 40 to 70 gigapascals and 1,000 to 2,000 kelvins, water consists of very short-lived molecules. Above 75 gigapascals and 2,000 kelvins, the water molecules are too short-lived to even be considered true molecules. Goldman says, "In this phase, the oxygen atoms form a lattice surrounded by a sea of mobile hydrogen atoms."

The superionic phase of water is important not only to planetary science but also to geosciences, fundamental chemistry, and weapons research. For example, Livermore researchers use computer codes to model detonation processes, which



(a) At room temperature and atmospheric conditions, hydrogen (H) and oxygen (O) atoms in water exist predominantly as traditional  $\text{H}_2\text{O}$  molecules. (b) At 2,000 kelvins and a million times atmospheric pressure, the atoms begin to cluster, and water is in a superionic phase.



occur at similar conditions to those in planetary interiors. Goldman says, "The superionic phase could possibly result from a detonation process, however short-lived the phase would be."

Because water is involved in nearly every aspect of life, scientists want to completely understand the thermodynamic properties of its many phases. Equipped with the power of Thunder and new algorithms using first principles, Livermore researchers are revealing the secrets of this ubiquitous substance.

—Gabriele Rennie

**Key Words:** Car-Parinello molecular dynamics (CPMD) code, classical molecular dynamics, density functional theory (DFT), first-principles molecular dynamics, hydrogen bonds, superionic phase, Thunder, water research.

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